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CHARACTERISATION OF PERMANENT MAGNETS FROM WEEE

N. MENAD*, A. SERON
BRGM – D3E/DMP, 3, avenue Claude Guillemin - BP 36009, 45060 Orléans cedex 02, France.
* Corresponding author: n.menad@brgm.fr. Tel: (33) (0) 2 38 64 47 37

Key words: Waste of electric and electronic equipments, magnets, thermal treatment, characterization

Abstract

The increasing use of rare earths elements in a number of recent technological innovations led to a rapid increase in (plus 50% in the last decade) of their applications. Europe is one of the most important regions of consumption of these substances. In this context, Europe in its ‘Raw materials’ strategy puts the recycling at the center of its concerns to provide a part of securing its supplies in rare earth elements. Recycling of these substances, on an industrial scale, remains somewhat developed while it presents numerous advantages over the exploitation of primary resources.

This paper will present some results obtained from characterization study of permanent magnets present in wastes of electric and electronic equipment. Three different electronic components containing magnets are identified: hard disk drives, small electric motors and speakers. Several kilograms of these wastes have been sampled at recycling plant. The representative sample has been dismantled manually to recover the magnets contained to quantify the amount of magnets in the investigated components. Thorough characterization results show that the weight percentage of magnets varies in the three investigated electronic components: 4.6% in the speakers, 2.5-2.8% in the hard disks, and between 0.8 and 2% in some electric motors.

The results of the thermal treatments of the magnets of the investigated samples show that the majority of these magnets lose their magnetic property upon reaching Curie temperature (300-400° C) in 15-20 minutes.

Scanning Electronic Microscopy (SEM) reveals the morphological aspects of these magnets which consist in crystals shaped tetrahedral phase Nd$_2$Fe$_{14}$B sintered in the presence of the interphase rich in rare earths elements (Nd, Dy and Pr). The magnets are layer coated with 20 µm thick. This layer consists in Ni, Zn or metals alloys. The chemical composition of some magnets obtained from EDS is close to theoretical composition of the standard magnet.
1. INTRODUCTION
The increasing use of rare earths elements (REEs) in a number of recent technological innovations led to a rapid increase in (more than 50% in the last decade) their applications. In this context, Europe in its 'Raw materials' strategy puts the recycling at the center of its concerns to provide a part of securing its supplies of REEs. Recycling of these substances, at the industrial scale, remains somewhat developed while it presents numerous advantages over the exploitation of primary resources:

- Europe is one of the most important regions of consumption of these substances. It has, in addition, accumulated during decades of consumer goods that arrived at end of life and are considered as secondary resources which could be extracted from the REEs.
- French and European dependency on resources from foreign countries can be reduced through the recycling of post-consumer waste;
- Treatment of secondary resources for the production of REEs would not cause no health and no environmental risks induced linked to the presence of processions of radionuclides from primary deposits;
- Production of metal resources through the use of secondary resources is most often done with energy consumption much lower than those observed for the exploitation of primary resources. It also expects that most recycling operations have an environmental benefit.

Thus, in order to increase the efficiency of the use of the REEs and decrease European dependence on these strategic elements, an effort to research and development should be made in all areas of their life cycle whether it is exploitation of ores (mineral processing, extractive metallurgy) or from the equipment at the end of life as the waste of electrical and electronic equipment WEEE.

This paper presents the work done with the project financed by French research agency in the frame of the contract ECO-TS deals with characterisation of permanent magnets present in electronic devices in order to recovery REEs contained.

2. RARE EARTH ELEMENTS
The rare earths market is private, reserved only for professionals and depends on supply and demand. These rare earths have no stock or State regulations instruments such as gold and oil market. Their prices are reported by the main world mines, representing the main stakeholders of rare earths in this case Chinese mines that monopolize the market. The rare earths are sold in different forms (oxide or metal) with 99% purity.

2.1. Application of REEs
In General, rare earths elements (REEs) are used in high technology, especially in the manufacture of high performance magnets, in phosphors present in color televisions or energy saving lamps, catalytic converters, batteries for mobile phones and magnetic alloys. REEs are also used in medical applications (medicines, ophthalmology, NMR, IRM, etc...). Table 1 groups their applications. It can be noted that the applications which consume more than 25% of REEs, are considered as major applications as shown in red color in table 1. As examples, we can say Samarium, neodymium, praseodymium, Gadolinium and Dysprosium which are the most used in the manufacture of permanent magnets.
Neodymium is one of the most abundant elements in WEEE. As shown in Figure 1, it is present in high quantity in different electronic devices. (Loudspeakers, HDD, LCDs, Tablet computers etc…).

As shown by Figure 1, the magnets can be found in different electronic devices with different concentrations of Neodymium (Nd). For example: computer contains in average 5.03 mg Nd: 2.4mg in HDD, 771 mg in CD-ROM and 310 mg in Loudspeakers; Laptop (4.45 mg Nd):1121 mg in HDD, 621 mg in CD-ROM and 626 mg in Loudspeakers; Tablet computer (347 mg Nd); Mobile-phone (46.4 mg Nd); Smartphone (120 mg Nd); Earphones (260 mg Nd) and LCD (3650 mg Nd).

<table>
<thead>
<tr>
<th>Device</th>
<th>Neodymium per device [mg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC</td>
<td>5.030</td>
</tr>
<tr>
<td>Hard disk drive (HDD)</td>
<td>2.441 (1.104-9.076)</td>
</tr>
<tr>
<td>CD-ROM</td>
<td>771 (319-3,236)</td>
</tr>
<tr>
<td>Loudspeaker</td>
<td>310</td>
</tr>
<tr>
<td>Laptop¹</td>
<td>4.447</td>
</tr>
<tr>
<td>Hard disk drive</td>
<td>1121 (851-1391)</td>
</tr>
<tr>
<td>CD-ROM</td>
<td>621 (447-794)</td>
</tr>
<tr>
<td>Loudspeaker</td>
<td>626 (550 – 703)</td>
</tr>
<tr>
<td>Tablet Computer</td>
<td>347</td>
</tr>
<tr>
<td>Mobilephone²</td>
<td>46.4 (14.3 – 115)</td>
</tr>
<tr>
<td>Smartphone²</td>
<td>120</td>
</tr>
<tr>
<td>Earphones</td>
<td>260 (38,9-955)</td>
</tr>
<tr>
<td>LCD-television</td>
<td>3650 (0.8– 7.4)</td>
</tr>
</tbody>
</table>

*Figure 1: Neodymium in electronic devices (Luise Westphal and Kerstin Kuchta)*

2.2. Magnets in WEEE
Since the development of powerful magnets (Nd-Fe-B) in 1980, the volume production of Neodymium has increased dramatically. This development permitted to improve significantly the performance of small engines and reduce the bulk and weight of portable electronic devices. As example, utilisation of miniaturized engines in mobile phones on the basis of small Nd-Fe-B type magnets for their vibration functions. These magnets are also very widely
used in the computer HDD where they constitute the engine, which ensures the positioning of the read/write heads. They allow to improving significantly the performance of this storage device and contributing to the reduction of the computer size. If the increase in the prices of rare earths elements has been relatively constant over the last decade, the technological revolution of developed countries made appear of the deficits of supply and the tensions that have resulted in a surge in prices since January 2010.

Despite the fact that the hard disk for computer market is doomed to continue its regression by 2017 (Figure 2), in general, the opportunities have been identified for hard disk drives. According to the literature, an overall increase of 11% by 2016 is expected on the market of hard disks (Figure 3).

**2.3. Production and market of magnet**

China is a larger producer of magnet in the world. In 2010, China and Japan produce about 50 Gg (50 000 t) and more than 10 Gg (10 000 t) of NdFeB type magnet respectively (Figure 4, A). However, the production of magnet in Europe and USA is lower than 14 000 t and 2 000 t respectively (Figure 4, B).

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**Figure 2:** Worldwide supply of Desktop and portable PCs, Portable PCs and Tablets forecast 2017

**Figure 3:** Evolution of the global market of hard disks - forecasts 2017 (Coughlin associates)

**Figure 4:** Production of NdFeB magnet in China and Japan (A), USA and Europe (B) (Xiaoyue Du and T.E. Graedel)
In 2012, the global demand of REEs for the manufacturing of permanent magnets is estimated around 25,500 t, approximately 21% of the worldwide demand which is about 120,000 t (Roskill, 2012). The demand for the magnets is very rapid increases (>150%) from 2000 to 2007 before decreasing to about 1/3 during the financial crisis between 2008 and 2009. The permanent magnets represent a very important market for REEs with a rapid increase in 2014. About 27K tons of rare earth oxides (REOs) have been consumed for the production of magnets representing 22% of total consumption.

As shown in light blue bar in the charts (Figure 5) the sales of neodymium-iron-boron (Neo) magnets are increasing exponentially. Sales of all permanent magnets were about $8 billion in 2005 and NeO alone will be sold over $17 billion in 2020 (Benecki, et al, 2010).

The NdFeB type magnets are the most commercialized in 2015. China is the country that consumes most REOs for magnet manufacturing. According to Roskill (2012), the global application of NdFeB magnets is expected to increase on average about 9% per year by 2020: 6-8% per year by 2016 with an acceleration from 2016 (Sofred Consultants, 2013). Demand will be driven by three sectors:

1. ICT: hard drives, mobile phone, DVD, etc. that contain low amounts of NdFeB magnets but are produced by mass (14000 t of magnets would have sold in 2012)
2. Electric motors (between 60 g and 350 g of NdFeB magnets by engine) in Asia primarily and hybrid and electric cars (approximately 2 kg of magnets per vehicle);
3. Wind turbines: current wind turbines use close to 600 kg of magnets per MW (direct drive), which corresponds to 155 Kg of neodymium and praseodymium Kg 27.5 per megawatt. The new generation of wind turbines will require much less reported power (165-250 kg of magnet/MW). However, the power of wind turbines to increase the size of the magnets will continue to grow and consequently the demand for rare earths. Some authors announce the figures of 2.3 tons of neodymium and 400 Kg of praseodymium by wind for 10 to 15 MW of power [report notes strategic CEIS, Matthieu Ahmed 2014].
The majority of the rare earth type magnet is manufactured in China (80%), 17% in the Japan and 3% in Europe. According to S. Contantinides, 2012, the change in the use of the magnet predicts a necessary increase of dysprosium by 80% between 2010 and 2015, while the requirement for neodymium will increase much less to approximately 54%.

3. MATERIAL AND METHOD

Three samples of hard disks drive (HDD), electric motors and loudspeakers were characterised in this work. More attention is given to HDD. After collection, the electronic devices containing magnets were subjected to sampling shown in figure 6. The working of specimen samples that can be defined as samples made without special precautions for HDD, the loudspeakers and electronic motors in the small electronic appliances were collected from various industrial plants. The characterisation of these specimens allowed us to define the minimum masses to be taken to ensure the representativeness of the samples and analyses. As noted, the magnets in these electronic products are very heterogeneous. One tonne of each product containing these magnets is required to perform the tests at the laboratory and pilot scales.

Figure 6 - Sampling of Hard disks at French Plant recycling company
4. RESULTS

4.1. Dismantling and magnet recovery

The representative samples of electronic components collected from industrial plant were sampled again for characterisation. As shown by figure 7, the bag containing laptop HDD contains about 70% of Laptop HDD and 30% computer HDD. However, the bag containing computer HDD consists of 98% of computer HDD and 2% others non-identified components.

<table>
<thead>
<tr>
<th>HDD/Laptop computer</th>
<th>Weight (kg)</th>
<th>Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDD laptop</td>
<td>97.7</td>
<td>69.6</td>
</tr>
<tr>
<td>HDD computer</td>
<td>41.5</td>
<td>29.5</td>
</tr>
<tr>
<td>Other Non</td>
<td>1.3</td>
<td>0.9</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>140.5</strong></td>
<td><strong>100.0</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>HDD/Computer</th>
<th>Weight (kg)</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>HD/Computer</td>
<td>179.3</td>
<td>98.1</td>
</tr>
<tr>
<td>Non identified</td>
<td>3.5</td>
<td>1.9</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>182.8</strong></td>
<td><strong>100.0</strong></td>
</tr>
</tbody>
</table>

Figure 7: Hard Disks drive representative sample

Two samples from hard drives of computers and laptop (Figure x) representing about 500 HDD were dismantled manually to recover the contained magnets. These magnets are then heated to 300 ° C between 15 and 20 minutes to demagnetize them. Each HDD is referenced by brand name, the year and the memory content volume. The samples are dismantled manually and all parts are weighted and the weight percent of the magnets contained each HDD is calculated. Furthermore, the recovered permanent magnets are characterised by Scanning Electron Microscopy (SEM) and chemical analyses.

A hundreds of loudspeakers and a few tens of small electric motors were collected from representative professional equipment (Figure 8). The characterization procedure performed is the same as that used for HDD.

Figure 8: Recovery of magnet from different electronic components of WEEE by manual dismantling
The results obtained from characterisation of computer HDD show that magnet represents about 3 Wt%, aluminium 80 Wt%, PCB 7 Wt%, plastics 1 Wt%, iron 8 Wt% and 1Wt% others (ceramics etc…) see Figure 9.

After dismantling of components containing rare earth type permanent magnets, the total fraction of electronic components containing permanent magnets was determined by weighing of all components and the only magnets was taking into a count for the determination of an average concentration magnet in each type of components. The results are presented in Figure 10. It can be seen, for central unit, the Wt% of magnet is varied from 1 Wt% to 6Wt% in average 3Wt%. However, for laptop, the Wt% of magnet is varied from 1 to 4Wt% in average 2.5 Wt%. Table 2 gives the weight percentages of magnets contained in other electronic components such as loudspeakers (4 – 6 Wt%) and electric motors (22 - 26 Wt% or 0.8 – 2 Wt%).

<table>
<thead>
<tr>
<th>Sources</th>
<th>Weight % of magnet in average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Computer loudspeakers</td>
<td>4 – 6</td>
</tr>
<tr>
<td>HDD from central unit computer</td>
<td>2.5 - 2.8</td>
</tr>
<tr>
<td>HDD from Laptop</td>
<td>2 - 3</td>
</tr>
<tr>
<td>Small electric motors (A)</td>
<td>22 – 26</td>
</tr>
<tr>
<td>Small electric motors (B)</td>
<td>0.8 – 2</td>
</tr>
</tbody>
</table>

Table 2: Weight percent of magnet in different electronic components
4.2. **Determination of demagnetisation temperature**

To determine the temperature which the magnet loses its magnetic properties, the test of TG/DTA was carried out on the permanent magnet recovered from electronic devices. The results are shown in Figure 11. This figure shows the thermal behaviour of permanent magnets of HDD and loudspeakers in the temperature range of 50 to 500°C. It can be seen that the effect for loudspeakers permanent magnet is at 459°C, this can be attributed to the Curie temperature of ferrite magnets. However, for HDD, two effects are observed. The first one is started at 145°C, which is attributed to their temperature utilisation, and the second one at 297°C. This temperature is attributed to the Curie temperature of the rare earth type magnets at which they lose their magnetic properties. Then, to demagnetize the NdFeB and ferrites type magnets, it must be heated, respectively, at the temperatures around 300°C and 500°C.

![Figure 11: TGA of permanent magnets of HDD and loudspeakers.](image)

The collected samples of loudspeakers and electronic motors are heterogeneous in point of view of type of magnet contained. To select those interested samples, X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) were carried. Figure 12 shows the XRD patterns of loudspeakers and electric motors. From this figure, it can be seen that not all permanent magnets present in the collected samples of electronic devices contain NdFeB type magnet.
4.3. Physical-chemical characterisation of Nd-Fe-B type magnet

To understand the morphology, the texture and the composition of the Nd-Fe-B magnets covered by this study, a characterization by scanning electronic microscopy (SEM) was conducted. The texture of these magnets consists of sintered crystals of Nd$_2$Fe$_{14}$B phase tetrahedral shape and a rich rare earth (Nd, Dy, Pr) at interphase see EDS in figure x.

Figure 13 shows that the Ni or Zn protective coating of magnet consists of a layer of approximately 20 µm thick. The morphology aspect of the same magnet observed from a polished section that lets appear the small size of grain. Some of them are filled with a mixture of rare earths and other almost nonexistent because of a sintering performance(Figure 14). The analysis conducted by EDS (Energy Dispersive Spectroscopy) on the magnet constituents is similar to that obtained theoretically by calculation from the formula Nd$_2$Fe$_{14}$B (Table 3). The analysis performed on tetrahedral grains confirms their composition of Fe, Nd and Pr and the composition of interphase which is rich in rare earth (Nd, Pr, Dy).
The elementary maps made by EDS on a polished section of a HDD magnet are presented in Figure 15. These maps indicate, as expected, the presence of two phases which are respectively the majority Nd$_2$Fe$_{14}$B alloy (red phase, 91%) and rich in REEs (inter-granular phase (blue phase, 9%). The oxygen is predominantly present in the inter-granular areas in association with Pr and Dy. Nd and Fe are predominantly present in tetrahedral phase grain Nd-Fe-B.

![Image of EDS maps showing Fe, Nd, O, Pr, Dy distribution on a HDD magnet](image)

**Figure 15: Textural and chemical Characterization of a HDD permanent magnet after demagnetization**

The permanent magnets that we are looking for contained Nd-Fe-B doped with Dy and Pr, and the chemical composition is shown in table 3.

<table>
<thead>
<tr>
<th>Nd$<em>2$Fe$</em>{14}$B magnet</th>
<th>Fe</th>
<th>Nd</th>
<th>Dy</th>
<th>Pr</th>
<th>Ni</th>
<th>B</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analysed (EDS)</td>
<td>64.4</td>
<td>24.1</td>
<td>1.4</td>
<td>4.0</td>
<td>1.0</td>
<td>1.1</td>
<td><strong>96.0</strong></td>
</tr>
<tr>
<td>Calculated</td>
<td>72.0</td>
<td>27.0</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>1.0</td>
<td><strong>98.0</strong></td>
</tr>
</tbody>
</table>

*Table 3 - Chemical composition of magnet from computer hard disks, %*
5. CONCLUSIONS

1. Identification of deposits of the magnets present in WEEE, and focusing on hard drives, small electric motors and speakers, we take into account 98% of the magnet field receivable in the small electronic appliances feed. The rest of the present magnets in this stream is disseminated in other equipment such as phones fixed, mobile, internet box... more difficult recoverable.

2. Two sampling campaigns were conducted on two different sites of industrial plant to collect a representative sample of hard drives and the loudspeakers.

3. The characterization study shows that the weight percent of magnets varies in the three investigated targets: 4 - 6% in the loudspeakers, 2.5 - 2.8% in the hard disks of station unit of computers, 2 - 3% in the laptops, and between 0.8 and 2% in small electric motors.

4. Scanning electron microscopy (SEM) shows that the magnets containing rare earth elements present in WEEE consist of Nd-Fe-B alloy in a tetrahedral form with an interface rich in REEs (Nd, Dy and Pr). About 20 µm thick coating layer consists of Ni, Zn or an alloy of Cu / Ni.

5. According to the XRD, the permanent magnets present in WEEE contain not only REEs, but also ferrites.

6. The Curie point at which the magnets lose their magnetic properties was determined by TGA for different investigated samples of magnets. The results show that the temperature utilisation of NdFeB type magnet is around 150°C and Curie point is about 300°C. However the ferrite magnet loses its magnet property at about 500°C.

REFERENCES


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